

PATENT SPECIFICATION

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(54) HYDROPHILIC POLYMER COATING FOR WATERCRAFT

(71) We, NATIONAL PATENT
 DEVELOPMENT CORPORATION, of 375
 Park Avenue, New York, New York, United
 States of America — a corporation organized
 and existing under the Laws of the State of
 Delaware, United States of America, do here-
 by declare the invention, for which we pray
 that a patent may be granted to us, and the
 method by which it is to be performed, to be
 particularly described in and by the follow-
 ing statement:—

The present invention relates to drag re-
 ducing coatings for watercraft.

It is an object of the present invention to
 reduce the resistance or drag developed on
 moving watercraft through water.

It has been found that this object can be
 achieved by using coatings, e.g. having a
 thickness of 0.3 to 5 mil, comprising film
 forming polymers which have the ability to
 absorb water, but which are insoluble in
 water, and remain intact, swollen on the
 surface thereby coated, as coatings on the
 underwater portion of watercraft.

Many conventional water-soluble polymers
 are useful in the practice of this invention, if,
 after application to the surface they are cross-
 linked to render them insoluble. The optimum
 amount of water absorption to obtain maxi-
 mum drag reducing effect varies somewhat
 with the composition of the polymer, film
 thickness, etc., but in order to be effective
 the polymer must absorb a minimum of 10%
 by weight of water. Preferably, it should
 absorb 20% of water to 120%, and it can
 absorb even more, e.g. 500% or 2,000% by
 weight.

The term marine coating is used in the

present description to cover coatings for
 watercraft. The term watercraft includes mov-
 able boats of all kinds, including, but not
 limited to sailboats, yachts, inboard and out-
 board motor boats, rowboats, motor launches,
 canoes, Kayaks, water skis, surf-boards, ocean
 liners, tugboats, tankers and other cargo ships,
 submarines, both of the atomic and conven-
 tional varieties, aircraft carriers, destroyers,
 etc. The underwater surface can be made of
 wood, synthetic resin material, bonded glass
 fibres, or other serviceable material.

The compositions may contain antifoulant
 agents and are then useful as coatings to
 render the watercraft resistant to fouling by
 marine organisms such as barnacles, algae,
 slime, acorn-shells (Balanidae) goose mussels
 (Lepadoids), tube-worms, sea moss, oysters,
 brozoans, tunicates, etc.

It is critical that the hydrophilic polymer
 should be water insoluble, or be rendered
 water insoluble, since otherwise it will not be
 permanently affixed to the underwater sur-
 face.

The coatings employed in accordance with
 the invention effectively reduce the "drag" or
 resistance developed on moving the coated
 surface through water.

It is desired to employ the coating
 solely to effect friction reduction on racing or
 pleasure craft, for example, which do not
 remain static in water for extended periods,
 it is not necessary to incorporate an antifoul-
 ing agent.

While not being bound by any theory it is
 believed that the mechanism of friction re-
 duction is two-fold. The coating absorbs a
 substantial percentage of water and the water

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swollen coating exhibits a low contact angle with the water. In addition, the swollen coatings are sufficiently soft (particularly if a linear polymer is employed) to provide a hydrodynamic damping effect and reduce turbulence of the flow.

The coatings employed in accordance with the present invention may comprise water-insoluble hydrophilic polymers or copolymers of the following, provided that they are not copolymers with hydroxyalkyl acrylates or methacrylates: unsaturated amines, p-aminostyrene, o-aminostyrene, 2 - amino - 4 - vinyltoluene, alkylamino alkyl acrylates and methacrylates, e.g. diethylaminoethyl acrylate, diethylaminoethyl methacrylate, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, t-butylaminoethyl acrylate, t-butylaminoethyl methacrylate, piperidinoethyl acrylate, piperidinoethyl methacrylate, morpholinoethyl acrylate, morpholinoethyl methacrylate, 2-vinylpyridine, 3-vinyl pyridine, 4-vinyl pyridine, 2 - ethyl - vinyl - pyridine, dimethylamino propyl acrylate, dimethylamino propyl methacrylate, dipropylaminoethyl acrylate, dipropylaminoethyl methacrylate, di - n - butylaminoethyl acrylate, di - n - butyl aminoethyl methacrylate, di-sec. butylaminoethyl acrylate, di-sec. butylaminoethyl methacrylate, dimethylaminoethyl vinyl ether, diethylaminoethyl vinyl sulphide, diethylaminoethyl vinyl ether, aminoethyl vinyl ether, aminoethyl vinyl sulphide, monomethylaminoethyl vinyl sulphide, monomethylaminoethyl vinyl ether, N - (gamma - monomethylamino) propyl acrylamide, N - (beta - monomethylamino) ethyl acrylamide, N - (beta - monomethylamino) ethyl methacrylamide, 10-aminodecyl vinyl ether, 8-aminooctyl vinyl ether, 5-aminopentyl vinyl ether, 3-amino-propyl vinyl ether, 4-aminobutyl vinyl ether, 2-aminobutyl vinyl ether, monoethylaminoethyl methacrylate, N - (3,5,5 - trimethylhexyl) aminoethyl vinyl ether, N-cyclohexylaminoethyl vinyl ether, 2 - (1,1,3,3 - tetramethylbutylamino) ethyl methacrylate, N - t - butylamino - ethyl vinyl ether, N - methylimino - ethyl vinyl ether, N - 2 - ethylhexylaminoethyl vinyl ether, N - t - butylaminoethyl vinyl ether, N - t - octylaminoethyl vinyl ether, 2-pyrrolidinoethyl acrylate, 2-pyrrolidinoethyl methacrylate, 2-aminoethyl acrylate, 2-aminoethyl methacrylate. The presently preferred amino compounds are alkylaminoethyl acrylates or methacrylates, most preferably, t-butyl- aminoethyl methacrylate.

While linear polymers (including both homo and copolymers) are preferred when the hydrophilic resins are used only to reduce the resistance on moving a coated watercraft surface through water there can also be employed cross-linked hydrophilic copolymers. Such cross-linked copolymers are frequently advantageously employed when antifouling agents are included in the composition to

provide more durable adherence to the underwater structure.

Preferably, the cross-linking agent is present in an amount of 0.1 to 2.5%, most preferably, not over 2.0%, although from 0.05 to 15%, or even 20%, of cross-linking agents can be used. All percentages, parts and proportions given herein are by weight unless otherwise stated. Of course, care should be taken that cross-linking agents are not used in an amount which renders the product incapable of absorbing at least 10%, or preferably 20%, of water.

Typical examples of cross-linking agents include ethylene glycol diacrylate, ethylene glycol dimethacrylate, 1,2-butylene dimethacrylate, 1,3-butylene dimethacrylate, 1,4-butylene dimethacrylate, propylene glycol diacrylate, propylene glycol dimethacrylate, diethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, divinyl benzene, divinyl toluene, diallyl tartrate, allyl pyruvate, allyl maleate, divinyl tartrate, triallyl melamine, N,N'-methylene bis acrylamide, glycerine trimethacrylate, diallyl maleate, divinyl ether, diallyl monoethylene glycol citrate, ethylene glycol vinyl allyl citrate, allyl vinyl maleate, diallyl itaconate, ethylene glycol diester of itaconic acid, divinyl sulphone, hexahydro - 1,3,5 - triacryl-triazine, triallyl phosphite, diallyl ester of benzene phosphonic acid, polyester of maleic anhydride with triethylene glycol, polyallyl glucose, e.g. triallyl glucose, polyallyl sucrose, e.g. pentaallyl sucrose, sucrose diacrylate, glucose dimethacrylate, pentaerythritol tetraacrylate, sorbitol, dimethacrylate, diallyl aconitate, divinyl citraconate diallyl fumarate.

There can be included, as co-monomers, ethylenically unsaturated acids or salts thereof such as acrylic acid, cinnamic acid, carotonic acid, methacrylic acid, itaconic acid, aconitic acid, maleic acid, fumaric acid, mesaconic acid and citraconic acid. Also, as previously indicated there can be used partial esters such as mono 2-hydroxypropyl itaconate, mono 2-hydroxyethyl itaconate, mono 2-hydroxyethyl citraconate, mono 2-hydroxypropyl aconitate, mono 2-hydroxyethyl maleate, mono 2-hydroxypropyl fumarate, monomethyl itaconate, monoethyl itaconate, mono Methyl Cellosolve ester of itaconic acid (Methyl Cellosolve is the monomethyl ether of diethylene glycol), Mono Methyl Cellosolve ester of Maleic acid. (The word "Cellosolve" is a registered Trade Mark).

The polymers can be prepared for use as casting syrups, as aqueous dispersions, by aqueous suspension polymerization or as solutions in organic solvents such as ethyl alcohol, methyl alcohol, propyl alcohol, isopropyl alcohol, formamide, dimethyl sulphoxide or other appropriate solvent.

Also, however, it is possible to use, in

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accordance with the present invention, coatings comprising the following: partially hydrolyzed polyacrylonitrile, water-insolubilized polyacrylic acid, polyvinyl alcohol, 5 water-insolubilized polyvinyl pyrrolidone, copolymers of vinyl pyrrolidone with other monomers, e.g. methyl methacrylate, cellulose ethers, preferably hydroxy C_1-C_4 alkyl cellulose ethers, e.g. hydroxymethyl cellulose, 10 hydroxyethyl cellulose, hydroxypropyl cellulose optionally partially hydrolyzed cellulose esters, preferably those of C_1-C_4 alkanolic acids, e.g. cellulose acetate having a degree of substitution of 1.3 to 2.3, cellulose acetate- 15 propionate and cellulose acetate-butyrate of similar degree of substitution, carboxymethyl cellulose, etc., vinyl acetate-vinyl alcohol copolymers (e.g. in the proportion 20:80 respectively), polymethylvinyl ether, polyethyl- 20 vinyl ether, polyurethanes formed by reaction of polyhydric alcohols such as glycerol, sorbitol, mannitol, pentaerythritol, trimethylolpropane $C_3H_7(CH_2OH)_3$, hexane 1,2,6-triol, mono or polysaccharides such as glucose, 25 sucrose, fructose and dextrin, tris dipropylene glycol phosphonate or tris dipropylene glycol phosphate with an amount of diisocyanate insufficient to react with all the hydroxyl functionality.

30 Such polyurethanes can have hydroxyl numbers of 100 to 500 and can be made from toluene diisocyanate, 4,4'-methylene bis (phenylisocyanate), oxydi (phenylisocyanate), 4 - methoxy - 1,3 - phenylene diisocyanate or any other conventional diisocyanate or 35 higher polyisocyanates such as those mentioned in U.S. patent 3,127,373. There can also be used polyurethanes formed by reaction of hydroxyl terminated polyesters with such polyisocyanates providing the hydroxyl groups are in excess. Examples of such poly- 40 esters are polyethylene sebacates, the reaction product of an excess of 1,4-butanediol with adipic acid and a small amount ($2\% \pm 1\%$) of trimethylolpropane of molecular weight 45 3,000 to 12,000, polyethylene glycol-propylene glycol adipate molecular weight 1,900, glyceryl adipate-phthalate. Likewise there can be used polyurethanes made by reacting such 50 polyisocyanates with hydroxyl terminated polyethers, e.g. from diethylene glycol, triethylene glycol, dipropylene glycol, polyethylene glycol with a molecular weight of 200 to 3,000, polypropylene glycol with a molecular weight of 200 to 3,000, tetramethylene 55 glycol with a molecular weight 200, 1,000 or 4,000, glycerol-propylene oxide adducts of molecular weight 265, 1,000 or 3,000, hexane 1,2,6-triolpropylene oxide adducts of molecular weight 500 to 4,000, or oxypropylated 60 sucrose. The hydroxyl numbers of such polyurethanes should be as indicated above.

Other suitable hydrophilic polymers include proteinaceous polymers such as casein 65 and gelatin; 3000-or-above molecular weight

polyalkylene oxides and imines, preferably C_2-C_4 alkylene oxide polymers (e.g. polyethylene oxide or polypropylene oxide) having a molecular weight of 3,000 or above, 70 preferably at least 5,000, and polyelectrolytes other than resins having hydroxyalkyl acrylate or methacrylate groups, such as polyitaconic acid, polyacrylic acid, vinyl alkyl ether-maleic anhydride copolymers, e.g. those wherein the vinyl alkyl ether is vinyl ethyl 75 ether, vinyl methyl ether or vinyl butyl ether, ethylene-maleic anhydride copolymers, styrene-maleic anhydride copolymers (preferably containing at least 30% maleic anhydride units), methyl methacrylate-maleic anhydride 80 copolymers, hydrolyzed ethylene-vinyl acetate copolymer containing at least 30% vinyl alcohol units, phenoxy resins, e.g. the phenoxy resin of molecular weight 30,000, see U.S. patent 3,305,526, col. 9, line 60 et seq., poly- 85 vinyl acetals containing free hydroxyl groups, e.g. polyvinyl formal-polyvinyl alcohol, polyvinyl butyral-polyvinyl alcohol.

Cross-linking of the applied coatings may be accomplished by a variety of techniques. 90 Curing of polymers containing hydroxyl functionality may be done using ammonium, potassium or sodium chromate or dichromate or other strong oxidizing agents, e.g. in an amount 0.2 to 5% of the solids. Titanates, 95 e.g. tetraisopropyl titanate, tetrabutyl titanate and tin compounds, e.g. stannous dodecanoate, stannous octoate can be used in like amounts. Polymers containing groups other than hydroxyl groups and having vinyl 100 unsaturation may be crosslinked by incorporation of free radical generators such as organic peroxides, e.g. sodium peroxide, hydrogen peroxide, ammonium or potassium persulphate, organic hydroperoxides, peracids, or 105 peresters.

Examples of suitable peroxy compounds include t-butyl peroctoate, benzoyl peroxide, isopropyl percarbonate, 2,4-dichlorobenzoyl peroxide, methyl ethyl ketone peroxide, 110 cumene hydroperoxide and dicumyl peroxide.

The inclusion of agents to create redox systems with the free radical generators aids in speeding the curing action as is well known in the art. 115

It is critical, as stated, to render the hydrophilic polymer water insoluble (if it is not already so) while at the same time not destroying the hydrophilic properties.

It is also critical that the hydrophilic 120 polymer form a continuous film outer coating on the watercraft, i.e. it should not be masked or blocked by a hydrophobic film former for example.

The hydrophilic polymer coatings employed 125 in accordance with the present invention can be coated over conventional antifoulants providing there is sufficient permeability that the bottoms of the watercraft are kept clean.

There also can be incorporated with the hydrophilic polymers in the coating compositions of the invention to provide coatings to prevent fouling by marine organisms any of the conventional inorganic or organic antifoulants including cuprous oxide, copper powder, mercuric oxide, cuprous oxide-mercuric oxide (e.g. in the proportions 3:1 respectively), mercurous chloride, organotin compounds including triphenyltin chloride, triphenyltin bromide, tri p-cresyltin chloride, triethyltin chloride, tributyltin chloride, phenyl diethyltin fluoride, tri (p-chlorophenyltin) chloride, tri (x-chlorophenyltin) chloride, dibutyl ethyltin bromide, dibutyloctyltin bromide, tricyclohexyltin chloride, triethyltin stearate, tributyltin stearate, triethyltin fluoride, tributyltin fluoride, diphenyl ethyltin chloride, diphenyl ethyltin fluoride, triphenyltin hydroxide, triphenyltin thiocyanate, triphenyltin trichloroacetate, tributyltin acetate, tributyltin neodecanoate, tributyltin neopentanoate, trioctyltin neodecanoate, tributyltin oxide, trioctyltin oxide, triphenyltin fluoride, tributyltin oleate, tripropyltin neodecanoate, tributyltin laurate, tributyltin octanoate, tributyltin dimethyl carbamate, tributyltin resinate, tributyltin chromate, amyl-diethyltin neodecanoate, tributyltin naphthanate, tributyltin isooctylmercaptoacetate, bis (tributyltin) oxalate, bis (tributyltin) malonate, bis (tributyltin) adipate, bis (tributyltin) carbonate, organo lead compounds, e.g. triphenyl lead acetate, triphenyl lead stearate, triphenyl lead neodecanoate, triphenyl lead oleate, triphenyl lead chloride, triphenyl lead laurate, triethyl lead oleate, triethyl lead acetate, triethyl lead stearate, trimethyl lead stearate, triphenyl lead bromide, triphenyl lead fluoride, organic compounds including 10,10' - oxy - bisphenoxazine, 1,2,3 - trichloro - 4,6 - dinitrobenzene, hexachlorophene, dichlorodiphenyl trichloroethane (DDT), phenol mercuric acetate, tetrachloroisophthalonitrile, bis (n-propylsulphonyl) ethylene.

The antifoulant is releasably entrapped in the hydrophilic polymer coating. The quantity of antifouling agent required in the coating, as would be expected, varies with the particular agent used and the severity of fouling tendency encountered in the particular service to which the coated vessel or static structure is to be used. In general, the amount of antifouling agent when employed will range from 2 to 200% of the resin by weight, although as little as 0.1% of antifoulant can be used based on the resin weight. The amount of anti-foulant should be insufficient to prevent the hydrophilic polymer from forming a continuous film.

Of course, there can be included in the formulation conventional pigments and fillers such as titanium dioxide, red lead, bone black, red iron oxide, talc, aluminum silicate, fullers

earth, pumice, zinc oxide, calcium carbonate, etc.

The coatings of the present invention can be applied to the surfaces to be subjected to underwater conditions from solution in organic solvents or from aqueous dispersions. Suitable solvents include lower aliphatic alcohols such as methanol, ethanol, propanol and isopropanol or mixtures of these solvents with higher boiling alcohols such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diacetone alcohol, n-butanol, sec. butanol, isobutanol and mixtures of these solvents with water. In some cases aromatic and aliphatic hydrocarbons, e.g. benzene, toluene, xylene and hexane can be used.

The coatings of the present invention generally exhibit adequate adhesion to marine surfaces protected by corrosion resistant finishes such as epoxy or vinyl based paints, to previously applied antifouling finishes and to polyester-fiberglass laminates. Typical of such finishes are those shown in Sparmann U.S. patent 2,970,923, Scott U.S. patent 3,214,279 and Robins U.S. patent 3,236,793.

The thickness of the coating applied will vary with the particular formulation employed and the method of application. It can be 0.1 mil. or more, e.g. from 0.1 mil. to 250 mils., in thickness. Usually it will be between 0.3 mil. and 5 mils. The coatings can be applied to the underwater surface, e.g. boat bottom or hull by any conventional procedure such as brushing, dipping, spraying or roller coating.

Coating applied at boat yards, marinas or similar locations will normally be placed in water soon after drying. These coatings if made from linear, alcohol soluble polymers will remain alcohol soluble. However, as pointed out *supra* it is also possible to provide cured or cross-linked coatings. These exhibit improved mechanical durability. There can be used the peroxide catalysts referred to *supra* alone, or as part of a 2-component catalyst system which is mixed into the coating solution immediately prior to application. Alternatively, the coating can be cured by incorporating a free radical initiator and heating the coated surface after drying.

Two component catalyst systems for effecting cure at ambient conditions, e.g. 20°C., include peroxides of the type referred to *supra* together with such amine accelerators as N,N-dimethylaminoethyl acetate, N,N-dimethyl aniline, N,N-dimethyl aminoethanol, N,N-dimethyl toluidine. The accelerator can be used in an amount of 0.05 to 1 part per part of peroxide, e.g. a mixture of 89% benzoyl peroxide and 11% dimethylaniline can be employed.

The invention will be understood best in connection with the drawing wherein:

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Figure 1 shows a boat having a coating according to the invention, and

Figure 2 is a cross-sectional view along the line 2—2 of Figure 1.

Referring more specifically to the drawing, the boat 2 in water 4 has a coating 6 of hydroxypropyl cellulose below the waterline 8. If desired, the entire boat can be coated with the polymer. The thickness of the coating 6 is greatly exaggerated for illustrative purposes.

A number of antifouling experiments were carried out using the hydrophilic polymers of the present invention. After six months of testing on polyester resin panels the best results were obtained using triphenyl lead acetate as an antifouling ingredient. The results were also superior to using the antifouling agent in formulations which did not include the hydrophilic polymer.

Most antifouling compositions now used on ocean-going vessels are based on the use of cuprous oxide pigment, an inert material. A large proportion of the cuprous oxide is not effectively used because it is encapsulated in the resin and is unavailable unless the resin itself breaks down. A second disadvantage of cuprous oxide is that it can induce galvanic corrosion. In addition, because of its dark color, it is unsatisfactory as an antifouling ingredient for decorative finishes.

The United States Navy is, of course, interested in antifouling finishes. It would like to have a 2-1/2 year minimum, but finds that cuprous oxide coatings last from 12—18 months. Another market for effective systems is on tankers and large freighters. The operators are constantly seeking ways to decrease fouling because even a small amount of extra drag on the hull makes an appreciable difference to the efficiency of the vessel, which has an important effect on the economics, particularly in tanker operations. In addition, there is a need for periodic removal from service for bottom cleaning.

During the past decade a number of organometallic and organic pesticides have been found to exhibit high activity against a broad spectrum of marine fouling organisms. Economic utilization of these chemical antifoulants in shipbottom formulations has not been successfully accomplished, however, primarily because of the encapsulation problem. The new anti-foulants are all several times more potent than cuprous oxide, but their relatively high cost dictates that they be employed at a fraction of the normal concentration of the latter cuprous oxide. Continuous contact between toxicant particles in the paint film is not maintained at these relatively low concentrations, so that the toxicants are not even utilized as efficiently as cuprous oxide, which in turn is also partially inactivated by encapsulation. Modification of the paints with inert extender pigments or

water-soluble resin constituents improves the efficiency of toxicant utilization, but degrades the physical integrity of the paint films to an intolerable degree. To date, the most successful compromise is represented by blends or organometallic anti-foulants with cuprous oxide to obtain durability and high potency. However, such blends eliminate the two major benefits offered by organic and organometallic antifoulants; freedom from the galvanic corrosion hazard of cuprous oxide, and flexibility of decorative pigmentation.

The use of hydrophilic water insoluble polymers of the present invention reduces the problem of encapsulation of anti-foulants in impermeable resin systems due to the water swellable nature of the hydrophilic film. There are certain other types of resin systems in which solid organic and organometallic anti-foulants do not demonstrate any significant activity unless their concentration in the film exceeds a threshold of 25% by weight of the resin, but in the coatings employed in accordance with the present invention activity at much lower concentrations is noticed indicating that the hydrophilic resin does not impermeably encapsulate the toxicant particles.

The following preparative and testing Examples illustrate the invention and its advantages. As mentioned above, all percentages, parts and proportions given herein are by weight unless otherwise stated. The abbreviation "phr" in the following Examples means "parts per hundred of resin".

Example 1

To a 10% aqueous solution of hydroxyethyl cellulose was added 1.18 phr. (based on polymer) of ammonium dichromate. A portion of the solution was coated on a pre-weighed glass slide and allowed to dry and cure at room temperature. The weight of the dried coating was then determined and it was placed in water over night. The coated glass was blotted free of surface moisture and weighed. The coating had swelled, picking up 397% of its dry weight of water.

A separate portion of the solution was used to coat the streamlined dart as described below for determination of drag reduction.

Example 2

Example 1 was repeated using hydroxypropyl cellulose in place of hydroxyethyl cellulose with 1.12 phr. of ammonium dichromate. The dried, cured coating swelled, picking up 590% of its weight on immersion in water for 18 hours.

Example 3

To a 10% solution of polyvinyl pyrrolidone in Ethanol was added 2 phr. of ammonium persulphate as a 10% aqueous solution.

The solution was coated on preweighed aluminium foil and allowed to dry at room temperature. The film swelled, picking up 15 times its dry weight of water after 18 hours of immersion.

Example 4

To a 10% aqueous solution of polyvinyl alcohol was added 2.36 phr. of ammonium dichromate. A dried film swelled picking up 58.7% of its weight of water on immersion for 23 hours.

Example 5 (Testing Example)

A 10 ft. vertical glass column, 6 inches in diameter was equipped with an axially located electromagnet at the top, an axially positioned guide line down the length of the column and photo-electric cells coupled with

a timing device at the bottom of the column. A streamlined aluminium dart having an axial hole through the centre was positioned over the guide line. The column was filled with water. The dart was held at the top of the column by the electromagnet. A single switch, which turned off the current to the magnet releasing the dart, simultaneously turned on the timer. The interruption by the falling dart of the light beam between the photocells positioned at the bottom of the column turned off the timer.

The dart was timed without having coatings applied thereto, and was then timed with various coatings applied to its surface.

The average results (10 trials) obtained with the uncoated dart and the dart with the coatings of Examples 4 are as follows:

	Coating	Surface Material	% H ₂ O in Film	Drop time (seconds)	Speed Increase %
	None	Aluminium		1.217	
40	Ex. 1	Hydroxyethyl Cellulose	403	1.183	2.8
	Ex. 2	Hydroxypropyl Cellulose	593	1.179	3.1
	Ex. 3	Polyvinyl Pyrrolidone	1520	1.180	3.0
45	Ex. 4	Polyvinyl Alcohol	57.8	1.176	3.4

In place of the hydroxyethyl methacrylate polymer solution of Example 1 of Specification No. 1303178 used to coat sailboats and motorboats, there can be used the hydroxyethyl cellulose solution of Example 1, the hydroxypropyl cellulose solution of Example 2, the polyvinyl pyrrolidone solution of Example 3, or the polyvinyl alcohol solution of Example 4.

Similarly, in place of the Hydron-S and the copolymers employed in Examples 11, 12 and 13 of Specification No. 1303178 there can be used the same weights of the polymers of Examples 1, 2, 3 or 4.

WHAT WE CLAIM IS:—

1. A watercraft having an adherent continuous exposed coating consisting essentially of a water-soluble hydrophilic polymer which is swellable to an extent of at least 10% by weight of the polymer by water, the said hydrophilic polymer being an optionally partially hydrolysed cellulose ester, a cellulose ether, a polyurethane, a polyvinyl C₁—C₄ alkyl ether, a —CH₂CHOH— containing polymer or copolymer, a polymer or copolymer containing vinyl pyrrolidone units, a polyelectrolyte other than a resin having hydroxyalkyl acrylate or methacrylate groups, a protein, a 3000-or-above molecular weight polyalkylene oxide or imine, or a phenoxy resin.

2. A watercraft according to claim 1 in

which the polymer is swellable to an extent of at least 20% by weight of polymer by water.

3. A watercraft according to claim 2 in which the polymer is swellable to an extent of up to 120% by weight of polymer by water.

4. A watercraft according to claim 1, 2 or 3 in which the coating has a thickness of 0.3 to 5 mil.

5. A watercraft according to any preceding claim in which an anti-fouling agent or a pigment is encapsulated in the polymer.

6. A watercraft according to any preceding claim in which underneath the said coating is an inner coating comprising an anti-fouling agent, the said coating permitting water to reach the said inner coating and permitting the anti-fouling agent to be gradually leached out.

7. A watercraft according to any preceding claim in which the polymer is normally water-soluble but has been cross-linked to render it water-insoluble.

8. A watercraft according to any preceding claim in which the polymer contains up to 20% by weight of a cross-linking agent.

9. A watercraft according to any preceding claim in which the polymer is a hydroxy C₁—C₄ alkyl cellulose ether.

10. A watercraft according to claim 9 in which the polymer is a hydroxy methyl cellulose ether.

11. A watercraft according to claim 9 in which the polymer is a hydroxy propyl cellulose ether.
- 5 12. A watercraft according to any of claims 1 to 8 in which the polymer is a carboxy-methyl cellulose.
- 10 13. A watercraft according to any of claims 1 to 8 in which the polymer is a partially hydrolyzed cellulose ester of a C_1-C_4 alkanolic acid.
14. A watercraft according to claim 13 in which the cellulose ester is a cellulose acetate.
- 15 15. A watercraft according to any of claims 1 to 8 in which the polymer is a hydroxyl-group containing polyurethane.
16. A watercraft according to any of claims 1 to 8 in which the polymer is polyvinyl alcohol.
- 20 17. A watercraft according to any of claims 1 to 8 in which the polymer is a hydrolyzed ethylene-vinyl acetate copolymer.
18. A watercraft according to any of claims 1 to 8 in which the polymer is a polyvinyl acetal.
- 25 19. A watercraft according to any of claims 1 to 8 in which the polymer is water-insolubilized polyvinyl pyrrolidone.
20. A watercraft according to any of claims 1 to 8 in which the polymer is water-insolubilized polyacrylic acid.
- 30 21. A watercraft according to any of claims 1 to 8 in which the polymer is partially hydrolyzed polyacrylonitrile.
- 35 22. A watercraft according to any of claims 1 to 8 in which the polymer is an ethylene-maleic anhydride copolymer.
23. A watercraft according to any of claims 1 to 8 in which the polymer is a styrene-maleic anhydride copolymer. 40
24. A watercraft according to any of claims 1 to 8 in which the polymer is a vinyl alkyl ether-maleic anhydride copolymer.
25. A watercraft according to any of claims 1 to 8 in which the polymer is a 3000-or-above molecular weight poly (C_2-C_4) alkylene oxide). 45
26. A watercraft having a coating substantially as hereinbefore described or exemplified otherwise than by way of acknowledgement of the prior art and of our Specification No. 1303178. 50
27. A method of treating a watercraft to reduce its resistance or drag, comprising applying to the watercraft below the waterline an adherent continuous exposed coating as specified in any of claims 1 to 25, or a coating as specified in claim 26. 55
28. The method of claim 27 substantially as hereinbefore described or specifically exemplified otherwise than by way of acknowledgement of the prior art and of our Specification No. 1303178. 60

For the Applicants,
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